Synthesis and fuel cell characterization of blend membranes from phenyl phosphine oxide containing flourinated novel polymers

CrossMark

Merve Gürtekin Seden [a], Emre Baştürk [b], Tülay Y. Inan [a, *], Nilhan Kayaman Apohan [b, *], Atilla Güngör [b, *]
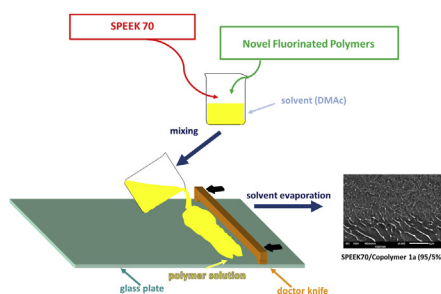
[a] TUBITAK, Marmara Research Center, Chemistry Institute, 41470 Kocaeli, Turkey
[b] Marmara University, Faculty of Art and Science, Department of Chemistry, 34722 Goztepe, Istanbul, Turkey

HIGHLIGHTS

- Blend membranes show high mechanical stability and good permeability to O_2 and H_2.
- Methanol permeability of blend membranes is much lower than Nafion® 117.
- The thermal stability of SPEEK70 is enhanced by blending up to 300 °C.
- Fluorinated polymer addition improves the chemical stability from 2.5 to 6.6 h.
- Blend membranes show lower water vapor permeability than that of Nafion® 117.

GRAPHICAL ABSTRACT

ABSTRACT

Novel fluorinated poly(arylene ether)'s are synthesized from polycondensation of bis (p-hydroxy-tetrafluoro) phenyl) phenyl phosphine oxide (PFPPO—OH) with 4,4′-dichlorodiphenyl sulfone (DCDPS) and 2,2-bis(4-hydroxyphenyl)propane (Bisfenol A) (Copolymer 1a) or 2,2-bis(4-hydroxyphenyl) hexafluoropropane (Bisphenol AF) (Copolymer 1b). The fluorinated copolymers have been blended with sulphonated poly(ether ether ketone)-SPEEK by solvent casting method. The water uptake and proton conductivity of the blend membranes decreases with the increase of copolymer content as expected, but proton conductivity values are still comparable to that of Nafion117® membrane. Addition of hydrophobic copolymer 1b to the SPEEK caused increase in water vapor transmission. Methanol permeability of the membranes is decreased to 8.2×10^{-8} cm^2 s^{-1} and 1.3×10^{-9} cm^2 s^{-1} by addition of Copolymer 1a and 1b, respectively and they are much lower than that of Nafion® 117 (1.21E-06 (cm^2 s^{-1}). The blend membranes endure up to 6.5 h before it starts to dissolve. Hydrogen and oxygen permeability of the blend membranes is one-hundredth of the Nafion®. Fluorinated polymer improved chemical, mechanical, and hydrolytic stability and also phenyl phosphine oxide structure in the ionomer increased the thermal stability, gas and methanol permeability and overcomed the drawbacks of the Nafion® type membranes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Proton exchange membranes composed of perfluorosulfonic acid polymers known as Nafion type membranes suffer from some drawbacks, such as high cost, low application temperature (<80 °C) and high methanol crossover [1–3]. To substitute the Nafion type perfluorinated ionomer membranes, the search for alternative proton-conducting polymer membranes has been intensified to a great extent in the last decade. Among the numerous alternative polymers, sulfonated polymers with arylene backbone such as poly (arylene ether ketone)s, poly (arylene ether sulfone)s and polyphenyleneoxide (PPO) are good candidates due to their superior acidic and high glass transition temperatures and excellent mechanical strengths [4,5]. However, it was shown that commercial polymers do not satisfy all of the requirements of fuel cell membranes, such as operation at high temperature, low methanol crossover, high mechanical and chemical durability in both the dry and hydrated state, high proton conductivity at as low as possible water uptake and economically reasonable production costs [6].

Currently, the efforts were strengthened in roughly three directions in order to approach the requirements to narrow the technical gaps between the current technology and the targets. One of the direction is to produce composite membranes by adding inorganic–organic and/or acidic–basic constituents. The water uptake of the membranes typically determines the proton conductivity and methanol permeation based on the ionomer microstructure, cluster and channel size [7]. Changing chemical structure of the polymer in the membrane is the second direction and thus the methanol crossover and other properties changes as well. Crosslinking of sulfonated polymers is the another reasonable method for improving the dimensional stability and avoiding the irreversible swelling of membranes while maintaining good proton conductivities [8]. Finally, the development of new (block-co)polymers with arylene backbone such as non-fluorinated and partially fluorinated poly arylene ethers (PAE), or polymers containing phenyl phosphine oxide unit was attempted [9].Among these structures, fully or partly fluorinated hydrophilic-hydrophobic multiblock copolymer ionomers are of particular interests since the fluorination of the hydrophobic segment is expected to promote nanophase separation with the hydrophilic segment, resulting in improved proton transport properties [10]. Although these ionomers designate a lower lifetime in fuel cells, they offer the possibility to be used in liquid fed fuel cells (such as DMFCs or DEFCs) which reduces the complexity of the fuel cell system significantly [11–13]. Thus to improve the chemical, thermal and hydrolytical stability of arylene main-chain polymers, fluorination is believed to be an effective and promising route, mainly due to the higher bond strength of the C–F bond compared to the C–H bond [14].

In particular, SPEEK was shown to have a lifetime of more than 3000 h [15], indicating SPEEK may be suitable for commercial production. Recently, proton-conducting blend membranes [16–21] in which SPEEK was used as a major component, have been explored with the goal to obtain good mechanical properties, high proton conductivity, and optimized membrane properties. The proton conductivity of SPEEK can be attained through the sulfonation process. However, the increasing degree of sulfonation (DS) leads to the elevated swelling in water or solvents. The SPEEK blended with poly(ether sulfone) [15] (PES), poly(ether imide) [18] (PEI) or polyvinylpyrrolidone [22] (PVP) has also been reported. Those membranes have been prepared to restrict the solvent absorption and to hinder the methanol flux.

In the present study, novel membranes were obtained with lower methanol crossover, lower gas crossover (H_2 and O_2) than Nafion membrane and higher oxidative stability, higher mechanical properties than SPEEK based other membranes in the literature by using SPEEK and novel partially florinated poly(arylene ether) based polymers. In order to promote nanophase separation, partially fluorinated PEEK selected with hydrophilic segment and higher bond strength of the C–F bond to improve proton transport, chemical, thermal and hydrolytic stability and overcome the drawbacks of the Nafion type membranes. In the novel ionomer we also included phenyl phosphine oxide structure in the ionomer to increase thermal stability and to decrease methanol and gas permeability values. The obtained membranes are candidates for PEMFC, DMFC and with the promising results of thermal and oxidative stability characterizations also may be the candidate for medium temperature PEMFC applications as well. In this paper, novel PFPPO–OH monomer was synthesized and using this monomer, 4,4′-dichlorodiphenyl sulfone and 2,2-bis(4-hydroxyphenyl)propane (Bisfenol A, 1a) and 2,2-bis(4-hydroxyphenyl) hexafluoropropane (Bisphenol AF, 1b) new co-polymers 1a and 1b were obtained. Obtained copolymers were then blended with SPEEK70 to produce membranes for fuel cell applications. All of the membranes were prepared by solution casting method in 15 w/v% concentrations in N,N-dimethylacetamide (DMAc). The effects of the type and contents of the novel synthesized fluorinated polymer on the membrane properties were investigated. The blend membranes were characterized by Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (^{1}H NMR), Differential Scanning Calorimetry (DSC) and ion exchange capacity (IEC). The surface topology of the blend membranes were investigated by a scanning electron microscopy (SEM). Thermal properties of the blend membranes were evaluated by thermogravimetric analysis (TGA). The water uptake, proton conductivity, methanol permeability, gas permeability and mechanical stabilities of the membranes were also investigated with the suitable methods.

2. Experimental

2.1. Materials

Phenylphosphonic dichloride and 4-bromofluorobenzene were purchased from Alfa Aesar chemical and used as received. Tetrahydrofuran (THF) was dried by refluxing over sodium wire. The solvent N,N-dimethylacetamide (DMAc, Fisher) was vacuum-distilled from phosphorus pentoxide onto molecular sieves. Potassium carbonate (Aldrich) was dried overnight in vacuum before copolymerization. Polyether ether ketone (PEEK) Victrex 450 PF obtained in powder form (particle size of 25 mm) from Victrex and was dried overnight at 100 °C under vacuum. Sulfuric acid (95–97% wt.), N,N-dimethylacetamide (DMAc, for synthesis) and hydrogen peroxide (H_2O_2) were purchased from Fluka. 2,2-Bis (4-hydroxyphenyl) hexafluoropropane (Bis AF), 2,2-bis(4-hydroxyphenyl)propane (Bis A) received from Aldrich, was purified by sublimation. Magnesium, potassium hydroxide, and other reagents were obtained from commercial sources and used without further purification.

2.2. Synthesis of 1,2-bis ((pentafluoro)phenyl) phenyl phosphine oxide (PFPPO)

1,2-Bis((pentafluoro)phenyl)phenyl phosphine oxide (PFPPO) was synthesized via Grignard reaction as described in the literature [23] with slight modifications. Phenylphosphonic dichloride (19.19 g, 0.096 mol) was added to the

pentafluorophenylmagnesium bromide solution, which was synthesized from Bromopentafluorophenyl (50.0 g, 0.20 mol) and magnesium (4.64 g, 0.19 mol) in dry THF (200 mL), over 30 min at room temperature with continuous stirring. Then the mixture was stirred further 4 h at 60 °C and was left overnight at room temperature. After the mixture was hydrolyzed with 7.5% sulfuric acid, the organic layer was collected by extraction with ether. The ether layer was washed with water and dehydrated with sodium sulfate. The residue obtained after the evaporation of ether phase and purification by bulb-to-bulb distillation in vacuo. Yield was 85%, mp 85–86 °C. Liquid chromatography–mass spectrometry (LC–MS): 459 [M+H]+, 481 [M+Na]+, 498 [M+K]+, IR (KBr, cm^{-1}): 1379 (P=O), 1269 (C–F), 3011 (aromatic –CH), 1465–1592 (aromatic C=C), 1221 (F–Ar). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 77.26–7.54 (s, 2H), 7.61–7.73 (s, 2H), 7.75–7.93 (s, 2H) [24].

2.3. Synthesis of bis ((p-hydroxy-tetrafluoro) phenyl) phenyl phosphine oxide (PFPPO–OH)

A round bottom flask (250 mL) equipped with a reflux condenser, stirrer, thermometer and nitrogen inlet, was charged with 12.09 g (0.026 mol) PFPPO, 80 mL 2 N KOH solution and 80 ml DMSO. The mixture was heated to 80–100 °C and the reaction was carried out until the solid phase dissolved completely (6 h) (Scheme 1). Then, 160 mL water was added and the mixture cooled to room temperature. Thus obtained crude, dark yellow colored, clear solution was filtered and the filtrate was then precipitated by dropwise addition into 0.01 N HCl solution. The solid phase was washed with water and dried at 70 °C in vacuum drying. Characterizations were done by FTIR, 1H NMR and mass spectroscopy. Yield was 65%. LC–MS spectrometry: 455 [M+H]+, 477 [M+Na]+, 494 [M+K]+, IR (KBr, cm^{-1}): 1397 (P=O), 1269 (C–F), 3011 (aromatic –CH), 1465–1592 (aromatic C=C), 1221 (F–Ar), 3019 (–OH). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.26–7.54 (s, 2H), 7.61–7.73 (s, 2H), 7.75–7.93 (s, 2H), 4.96–5.31 (s, 2H) (Figs. 1 and 2).

2.4. Copolymer preparation

Polycondensation reactions, especially for the polymerization of partially fluorinated polyarylethers, was described earlier by Mercer and Sovish. [25] The polymers 1a, and 1b were prepared according to this procedure and the preparation of polymer 1a is given below:

2,2-Bis(4-hydroxyphenyl)propane (Bis A; 4.47 g, 26.12 mmol), Bis (p-hydroxy-tetrafluoro) phenyl) phenyl phosphine oxide (PFPPO–OH; 2.97 g, 6.53 mmol), 4,4′-Dichlorodiphenyl sulfone (DCDPS; 7.50 g, 26.12 mmol), potassium carbonate (9.92 g, 71.57 mmol) and 120 mL of DMAc were added to a 250 mL round flask. The mixture was heated with stirring under argon to 80 °C for
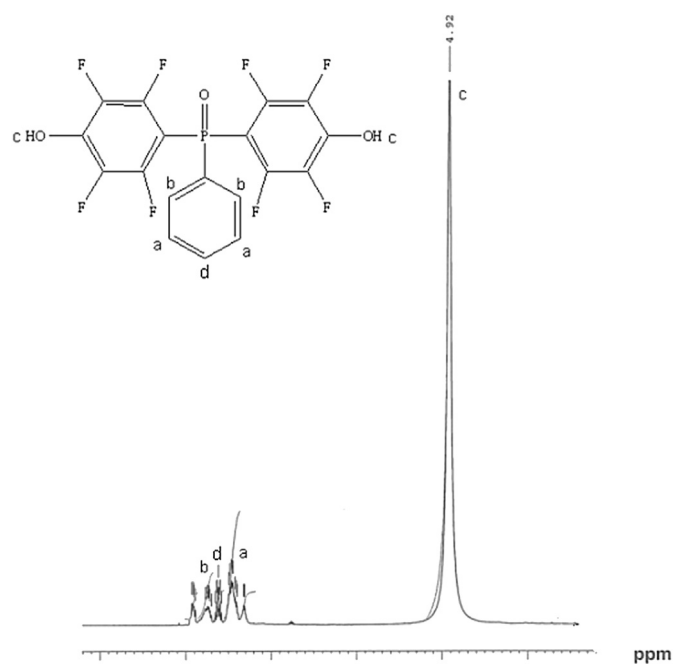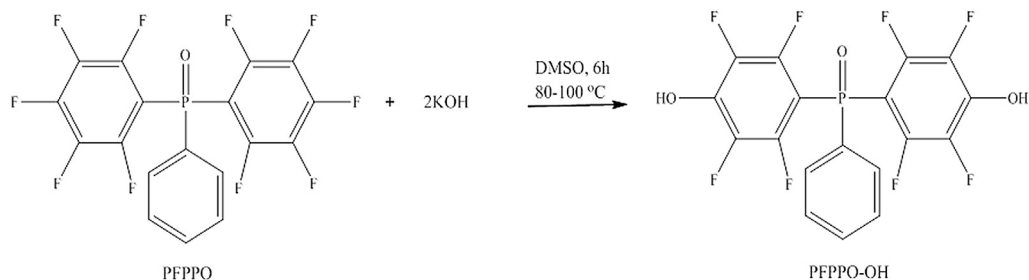

Fig. 1. ^{1}H NMR spectrum of PFPPO–OH.

23 h. Then the temperature was raised to 90 °C for 2 h and finally to 100 °C for another 2 h. The hot mixture was filtered to remove the unreacted potassium carbonate and potassium fluoride by-products. After the solution was cooled to room temperature, it was poured into 2000 mL of water to precipitate the polymer. The polymer was filtered, washed six times with water, and dried at 50 °C for 24 h. Characterizations of 1a and 1b were done by FTIR, ^{1}H NMR and DSC.

1a: IR (KBr, cm^{-1}): 1396 (P=O), 1282 (C–F), 3095 (aromatic –CH), 1584–1652 (aromatic C=C),1011 (symmetric S=O), 1089 (asymmetric S=O), 1158 (sulfone S=O), 1250 (C–O–C). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.84–7.89 (s, 4H), 7.84–7.88 (s, 2H), 7.45–7.52 (s, 3H), 7.47–7.49 (s, 2H), 7.06–7.11 (s, 2H), 6.99–7.03 (s, 2H), 6.89–6.95 (s, 2H), 6.71–6.77 (s, 2H), 1.75 (s, 6H), DSC: Melting temperature: T_m: 138 °C, Crystallization temperature: $T_c = 75$ °C, M_w (g mol^{-1}) = 3715.

1b: IR (KBr, cm^{-1}): 1396 (P=O), 1283 (C–F), 3096 (aromatic –CH), 1586–1616 (aromatic C=C), 1011 (symmetric S=O), 1089 (asymmetric S=O), 1158 (sulfone S=O), 1252 (C–O–C). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.94–8.01 (s, 4H), 7.95–7.99 (s, 2H), 7.66–7.73 (s, 3H), 7.67–7.70 (s, 2H), 7.21–7.23 (s, 2H), 7.18–7.21 (s, 2H), 7.08–7.13 (s, 2H), 6.78–6.85 (s, 2H). DSC: Crystallization

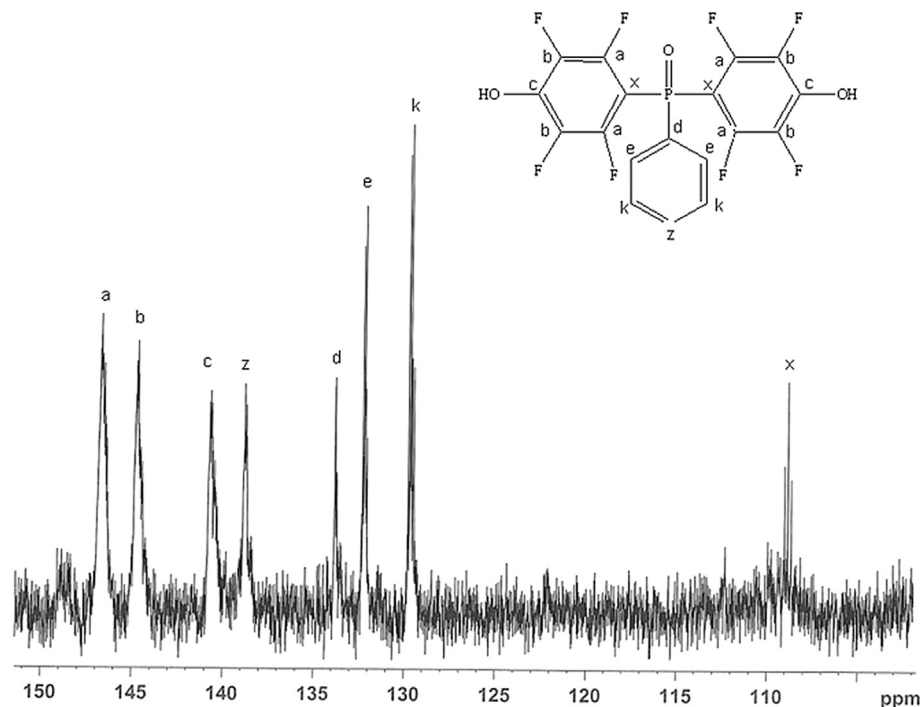**Scheme 1.** Schematic representation of PFPPO–OH reaction.

Fig. 2. ^{13}C NMR spectrum of PFPPO–OH.

temperature: $T_m = 128\,^\circ\text{C}$, M_w (g mol^{-1}) = 4673 (Figs. 3 and 4, Scheme 2).

2.5. Sulfonation of PEEK

Commercially available PEEK was sulfonated by using concentrated sulfuric acid (conc. H_2SO_4) as reported by Inan [21] and shown in Scheme 3.

A typical procedure for the sulfonation of PEEK is given as follows: 5 g dried PEEK and 100 mL of concentrated sulfuric acid (95–97%) were charged into a two-neck flask equipped with a mechanical stirrer 500 rpm and under nitrogen at 60 °C, 4 h. The reaction mixture was slowly poured onto 1 kg ice cubes and water mixture. The precipitate was filtered and washed with deionized water several times until the pH value was approximately 6–7. The sulfonated polymer samples were dried in vacuum at room temperature for 12 h and then at 60 °C for 12 h. The sulfonation degree (%) was obtained as 70 with IEC 2.02 meq g^{-1}.

2.6. Preparation of blend membranes

The blend membranes were prepared via the solution casting method. The indicated amount of copolymer and SPEEK were dissolved in DMAc having a concentration of about 15% w/v. The amount of copolymer in the blend was varied from 0 to 20 wt.%. Multi-stage membrane drying technique was applied until solvent was removed completely. Membranes were peeled off from the glass plate by immersing in deionized water. The thickness of SPEEK blend membranes was measured in the range of 70–110 μm by digital micrometer in their dry state. In this work, SPEEK70 denotes the blend membrane containing 70 wt.% sulfonation degree of the copolymer. To comparison, a piece of pure SPEEK membrane was prepared by the same method and was designated as SPEEK0.

2.7. Polymer and membrane characterization
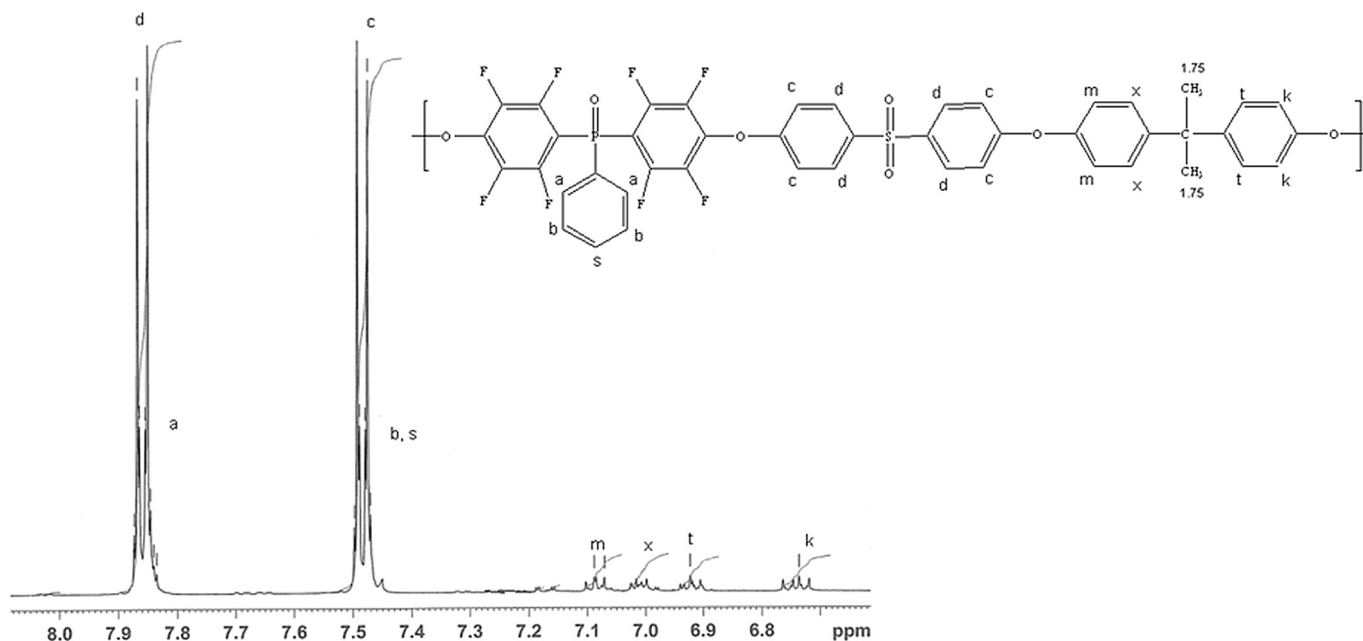
2.7.1. Instrumentation and methods

^{1}H NMR spectra were recorded on a Bruker NMR Spectrometer (500 MHz) in CDCl$_3$ (for PFPPO and PFPPO–OH) and DMSO-d_6 (for polymers) at room temperature. FTIR spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrometer. Differential scanning calorimetry (DSC) analyses were performed at a heating rate of 10 °C min^{-1} under nitrogen atmosphere using Perkin Elmer Jade DSC. Reported values were obtained from a second heating after a quick cooling of the first run. The proton conductivity of membranes was determined by using BT-512 BekkTech membrane test system at 100% relative humidity (RH) at 80 °C. Membrane morphology was investigated under a scanning electron microscope (JEOL 6335F). The SEM analysis was operated at 20 kV accelerating voltage. After dissolving with DMAc, very small drops of samples were dropped onto carbon support film coated copper TEM grids (Agar Scientific EMS). Transmission Electron Microscopy measurements were performed on JEOL-2100 HRTEM operating at 200 kV (LaB6 filament) and equipped with an Oxford Instruments 6498 EDS system. Images were taken by Gatan Model 694 Slow Scan CCD Camera.

2.7.2. Ion exchange capacity (IEC)

IEC values of membranes were calculated by titration method according to the previously reported procedure [26]. In this case, 0.1–0.2 g dried membrane sample was immersed into the 50 mL of saturated NaCl solution at 50 °C for 48 h to replace the sulfonic acid to the sodium salt form. The H$^+$ released from the membrane was titrated with a 0.1 N NaOH solution using bromothymol blue as an indicator.

2.7.3. Water uptake

Water uptake values of the polymer ionomer and their blend membranes were determined according to ASTM D570-98.

Fig. 3. ^{1}H NMR spectrum of copolymer 1a.

Membranes were conditioned in an oven first at 105 °C for 1 h and then at 50 °C for 24 h. The membranes were cooled to room temperature in a desiccator, immediately weighed and then soaked in deionized water at room temperature for 24 h. Then, the membranes were removed from water, wiped free of the water with a tissue paper and then weighed immediately (W_{wet}) again. The water uptake percentage (WU%) value was calculated by using the Equation (1):

$$WU(\%) = 100 \times \left(W_{wet} - W_{dry}\right) / W_{dry} \qquad (1)$$
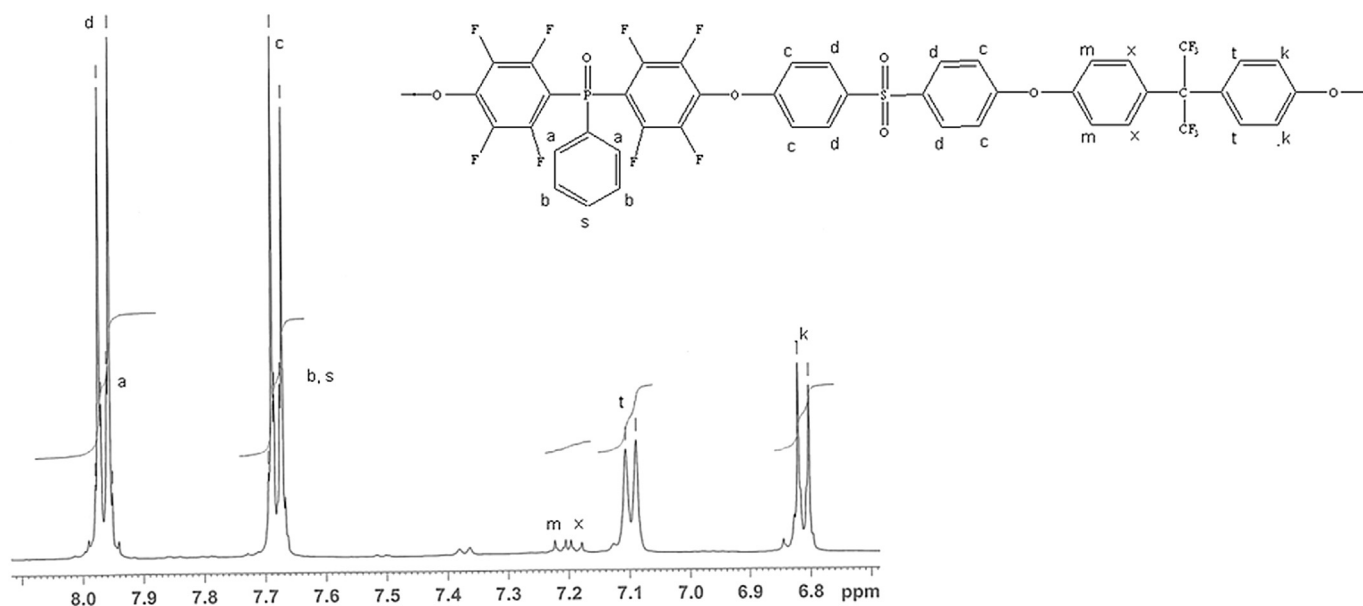
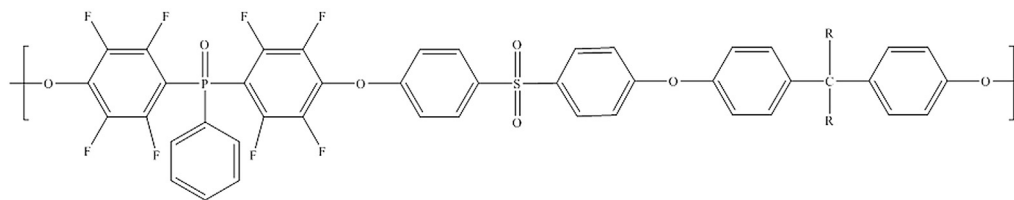where W_{dry} and W_{wet} are the weights of dry and wet membranes, respectively.

2.7.4. Oxidative stability

The membrane samples dried in a vacuum oven at 60 °C for 8 h, Fenton test was carried out according to the procedure described by Zhang and Mukerjee [27] in order to determine the chemical stability. Dried membrane samples were treated in 3% H_2O_2, which contained 4 ppm Fe^{2+} and then weight loss (wt.%) in 2 h and the rupture time (h) was reported.

2.7.5. Methanol permeability

Methanol permeabilities of the membranes were measured by using jacketed diffusion glass cell. The cell is composed of a two compartments glass cell with the membrane separating the two compartments .

Fig. 4. ^{1}H NMR spectrum of copolymer 1b.

R: -CH$_3$ (1a), -CF$_3$ (1b)

Scheme 2. Copolymer 1a and copolymer 1b which are composed of PFPPO–OH, DCDPS and Bis A or Bis AF.

The membrane was clamped vertically between two glass compartments. Magnetic stirring bar was used in each compartment for solution agitation. One of the compartments was filled with 45 mL, 2 M methanol solution and equal volume of distilled water was added to the other compartment after the desired temperature was reached. Both compartments were magnetically stirred during the permeation experiments. Methanol concentrations in the water cell were periodically measured by taking samples to be subsequently analyzed using a gas chromatography. The methanol diffusion coefficient was calculated with the following equation (Eq. (2)):

$$-\ln((2C_A/C_{A0}) - 1) = (2_{AM}D_{AB}) \times t/(V_0 \times \Delta x) \tag{2}$$

where A_M, Δx and V_0 are the effective area (4.15 cm^2), the thickness of membrane and the volume of permeated compartment, respectively. C_{A0} and C_A are the methanol concentration in methanol chamber and water chamber. D_{AB} is the methanol diffusion coefficient [28].

2.7.6. Gas permeability

The gas permeability properties of the blend membranes were evaluated according to ASTM D1434-82 and H$_2$ flow rate was calculated according to the following equation (Eq. (3)):

$$\text{Gas permeability} \left(\text{cm}^3_{STP} \times \text{cm} / \text{cm}^2 \times \text{s} \times \text{cm Hg} \right)$$
$$= V \times L / \left(A \times t \times \Delta P \right) n! / \left(r! \left(n - r \right)! \right) \tag{3}$$

where V is the volume of the permeated gas, A is the area of the membrane, t is the time, ΔP is the partial pressure difference of a gas between the feed and the permeating sides of a membrane and L is the membrane thickness.

2.7.7. Proton conductivity

Proton conductivities of the sulfonated membranes were determined by four-point probe method using In-plane membrane conductivity test system (BT-512 Model, BekkTech LLC, Loveland, CO). The sample membrane (approximately 4 mm × 30 mm) was connected with four probes: two outside platinum wires to apply the current and two inside platinum wires as reference electrodes.

Voltage–current values were set and measured by using the Keithley 2400 Sourcemeter. Sample was tested under different relative humidity between 30 and 100% at fuel cell operating temperature of 80 °C. Nitrogen gas was passed through the conductivity cell to obtain desired relative humidity. Four electrode conductivity (s) was determined from measured membrane resistance (R) by using following equation (Eq. (4)):

$$\sigma = L/R \times W \times T \tag{4}$$

where L is the distance (cm) between two reference electrodes, W and T are the width (cm) and thickness (cm) of the dried sample membrane, respectively.

2.7.8. Water vapor permeability

Water vapor permeability of the membranes was determined by means of water vapor transmission rate (WVTR). This test has been standardized by ASTM E 96-/E-96M-13. Membrane specimens (ø: 11 mm) were placed on the glass cups containing a certain amount of desiccant (anhydrous calcium chloride) and the membrane was secured in place with the help of clamp. The cups were placed in a desiccators containing sulfuric acid solution. The test was conducted with 50–55% relative humidity outside the cup and negligible relative humidity inside the cup. The value of relative humidity outside the cup was measured by hygrometer at 20–22 °C. The mass of the cup was recorded at 24 h interval for fortnight. Mass loss was plotted versus time and a straight line was obtained. Linear regression (linear regression coefficient >0.993) was used to estimate the slope of the line to calculate water vapor transmission rate as follows:
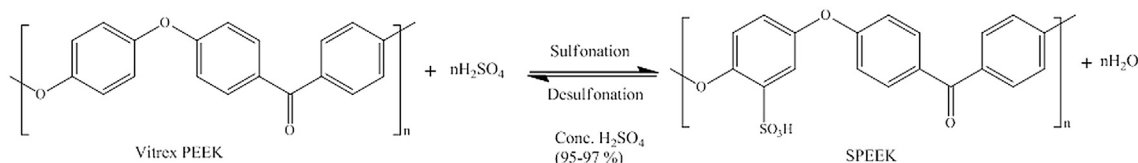
$$\text{WVTR} = \frac{\text{Slope}}{A}$$

where WVTR is the water vapor transmission rate (g m^{-2} day^{-1}) and A is the test cup mouth area (m^2).

Water vapor permeability is calculated by means of WVTR.

$$\text{WVP} = \frac{\text{WVTR} \times L}{S \times (R_1 - R_2)}$$

where S is saturation vapor pressure at test temperature, R_1 and R_2 relative humidity at the desiccators and vapor sink respectively.

Scheme 3. Schematic representation of PEEK sulfonation reaction.

2.7.9. Mechanical properties

Mechanical properties of the blend membranes were determined by standard tensile stress–strain tests to measure modules, ultimate tensile strength and elongation at break. Standard tensile stress–strain experiments were performed at room temperature on a Material Testing Machine Z010/TN2S, using a crosshead speed of 5 mm min^{-1}.

Mechanical properties of the blend membranes in 50–60% relative humidity condition under ambient temperature at 5 mm min^{-1} strain rate according to ASTM D 882-12 standard are presented and compared with Nafion 112 membrane measured at the same conditions in our previous article [21].

3. Experimental results and discussion

3.1. Sulfonation of PEEK

Concentrated sulfuric acid (95–97%) was used in this work for the PEEK sulfonation as depicted in Scheme 3. SPEEK polymers were obtained with 70% sulfonation degree (SD) and ion exchange capacity = 1.43 (IEC) in 4 h at 60 °C. FTIR is one of the methods used for the characterization of PEEK sulfonation (Fig. 6b). The intensity of absorption band at 3434 cm^{-1} increased due to the O–H stretching of SO$_3$H and absorbed moisture. Symmetrical vibration between sulfur–oxygen (O=S=O) was observed at 1080 cm^{-1}, O=S=O, S=O and S–O stretches were observed at 1255 cm^{-1}, 1075 cm^{-1} and 1020 cm^{-1} as a new band emerged while no change observed in the carbonyl band at 1649 cm^{-1} [29].

The ^{1}H NMR spectrum of SPEEK is given in Fig. 5. The presence of a sulfonic acid group causes a significant singlet signal (H_E) at 7.52 ppm.

3.2. Characterization of blend membranes

Blending techniques are an extremely promising approach which can improve the properties of the polymer. Blend membranes of fluorinated copolymers (1a and 1b) and SPEEK with sulfonation degree of 70 were prepared while the weight ratio of SPEEK/Copolymer was varied (100/0, 95/5, 90/10, 80/20).

3.2.1. FTIR analysis

Fig. 6 indicates the FTIR spectra of the pure SPEEK70, copolymer 1b and blend membrane (95/5). As seen in the spectrum of blend membrane, the absorptions from 1600 to 1450 cm^{-1} were attributed to the aromatic ring, and the absorption at 1242 cm^{-1} corresponded to the Ar–O–Ar. The peaks corresponding to the asymmetric stretching of P=O and C–F stretching cannot be distinguished in IR of blend membrane since they overlapped with SPEEK bands. In Fig. 6 the spectrum of blend membrane clearly shows the presence of C–H aromatic stretching band at 3095 cm^{-1}, symmetric S=O at 1011 cm^{-1} and asymmetric S=O at 1090 cm^{-1}.

3.2.2. Membrane morphology

The internal morphology of the membranes was studied by scanning electron microscope (SEM) as shown a, b, c, d, e, f and g in Fig. 7. Dense and defect free membranes were obtained by blending SPEEK70 with copolymer 1a (Fig. 7a–c) and copolymer 1b (Fig. 7d–f) in all ratios (5–20% wt/v). The similar morphology between blend membranes and neat SPEEK membrane reflected that no obvious macroscopically phase separation occurred. This is due to the good miscibility between copolymer structure and SPEEK. EDS analysis of SPEEK70/Copolymer 1a (80/20) blend was performed and the results are given in Fig. 8. The analysis results clearly show that, the gray part of the micrographs mainly contains S, C and O elements coming from SPEEK70 polymer and copolymer. However the bright regions are fluorine rich in addition to others. It is known that the areas reflecting lots of electrons appear bright in SEM.

TEM-EDS analysis results are given in Fig. 9a–b. Blend membranes which were coded as a and b, have sulphonated polymer SPEEK and Bis A and Bis F derivatives of flourinated copolymers, respectively in their structures. Flourinated copolymer b has higher fluorine content in its repeat unit than copolymer a which means b is more thermodynamically immiscible due to their dissimilar structures [21]. As seen from figures both blends have large, isolated ionic domains (the dark areas) that are approximately 100 nm in diameter. On the other hand the uniform bright backgrounds represent hydrophobic domains consists of flourinated copolymer and aromatic backbone of SPEEK70 [30–32].

3.2.3. TGA and DSC analysis

Polymer properties such as thermal stability and glass transition temperature (T_g) are important parameters for fuel cell applications. It is preferred that T_g and the thermal stability of polymers used as materials in low and intermediate temperature fuel cells
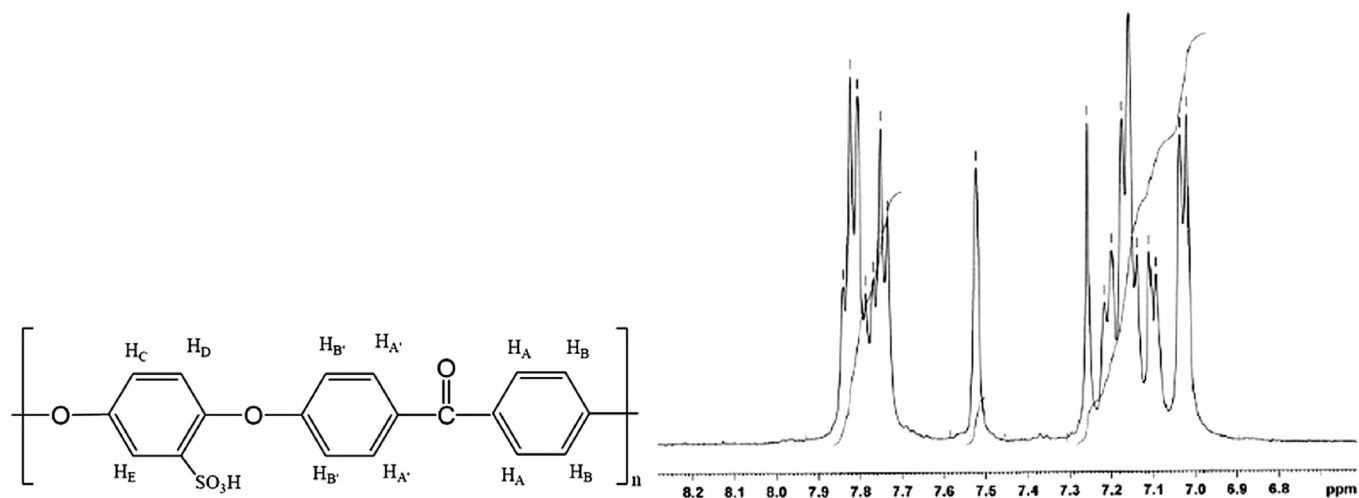
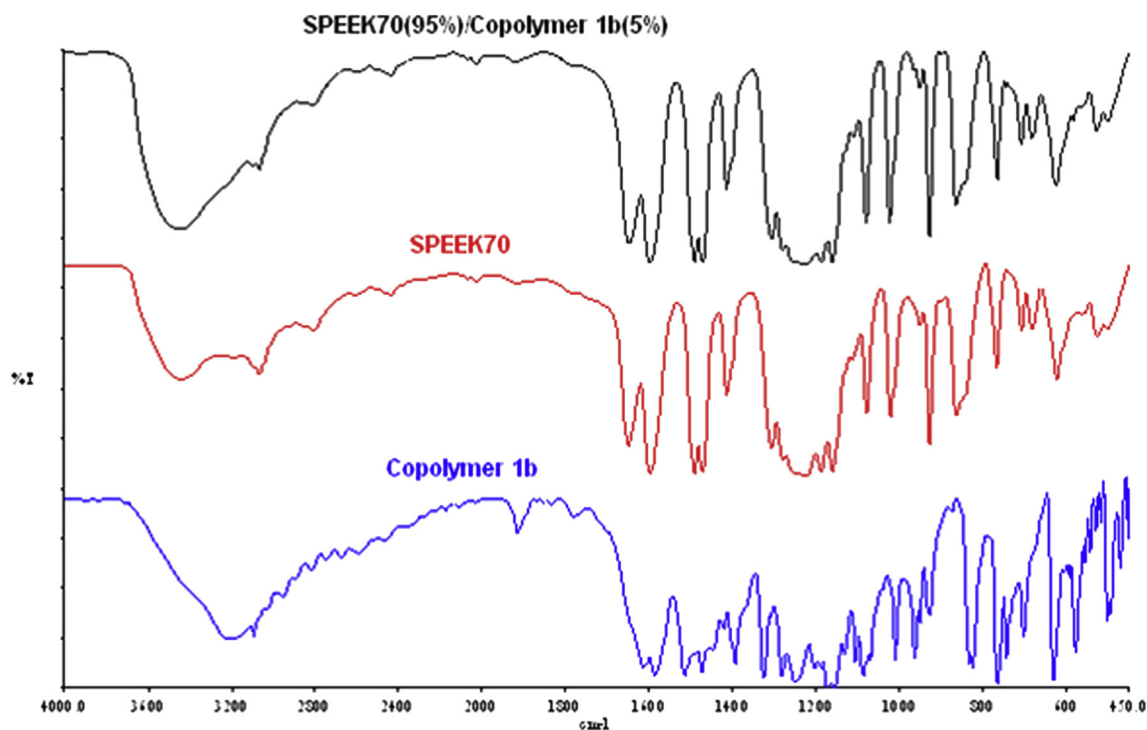

Fig. 5. ^{1}H NMR spectrum of SPEEK.

Fig. 6. FTIR spectra of the copolymer 1b, SPEEK70 and blend membrane (95/5).

(LTFC, ITFC) should be as high as possible since softening and thermal degradation of the ITFC materials in the range of the intended application temperature from 80 to 120 to 200 °C should be avoided. Fig. 10 illustrates the thermogravimetric analysis of the blend membranes with various compositions. For all blend membranes, four major weight loss stages were observed. The first weight loss was attributed to the splitting-off of the sulfonic acid groups. The others were the degradation steps corresponding to decomposition of the main chain. The blend membranes exhibited lower thermal stability than the pure SPEEK70 membrane. As shown in Fig. 10, with the increase of copolymer 1a or 1b content from 5 to 20%, the maximum weight loss temperature decreased from 365 to 315 °C due to the low molecular weights of the copolymers. In fuel cell membranes, two major factors may compete with each other to affect the thermal stability. First, the increase of sulfonated polymer content leads to the incorporation of more sulfonic acid groups and consequently the thermal stability decreases [33,34]. Contrary to this, when the polymer chains are crosslinked, the polymer cohesion and ordering increase, which results in the increase of thermal stability [35]. In this study, incorporation of the lower molecular weight of the novel synthesized copolymers and decreased amount of sulfonated polymer of SPEEK70 in the blend compositions are the dominant factors on thermal stability of the blend membranes. Although the addition of Copolymer 1a, 1b causes the membrane to decompose at relatively low temperature, the thermal stability of blend membranes is still good enough to serve as the PEMs in DMFCs. Moreover it is known that, while burning, the phosphorus rich residue form a glassy layer above the coating and this inhibits the oxygen transfer through the polymer bulk and also limits the production of combustible carbon-containing gases. As seen in Fig. 10a–b phosphorus groups which are degrading at relatively low temperatures forms a protective coating and increased the thermal stability of blend membranes up to 300 °C, compared to SPEEK.

Fig. 11 displays DSC curves of blend membranes. In Fig. 11a and b, the T_g values of SPEEK70/Copolymer 1a and SPEEK70/Copolymer 1b Blends are presented, respectively. T_g value of SPEEK70 is 173 °C. The T_g values of blend membranes with copolymer 1a decreased from 159 to 133 °C and whereas with copolymer 1b decreased from 156 to 147 °C as the copolymer contents increased from 5 to 20% respectively. The decrease in T_g was lower for copolymer 1b incorporated blend membranes since its molecular weight was higher than copolymer 1a ($M_{w(copolymer1a)}$(g mol^{-1}): 3715, $M_{w(copolymer1b)}$(g mol^{-1}): 4673). The thermal stability of all batches, determined via TGA, is very similar. Therefore, from the point of view of glass transition temperatures, it can be concluded that there is a strong preference for choice of polymers having higher M_w.

3.2.4. Ion exchange capacity, proton conductivity, and water uptake

The ion exchange capacity (IEC) is a physical quantity to represent the amount of the exchangeable protons in the ionomer membranes. The values of IEC are compiled in Table 1. The experimental values of IEC are in a range of 0.74–1.43 meq g^{-1}.

The proton conductivity (at $T = 80$ °C and RH = 100%), IECs and water uptake values of blend membranes having different Copolymer 1a and 1b content are shown in Fig. 12 and Table 1. The proton conductivity significantly depends on the degree of the hydration and the surrounding temperature. Therefore, before proton conductivity measurement, all the membrane samples were soaked in water at room temperature for hydration. Addition of Copolymer 1a and 1b to the SPEEK in 5–20 wt.% caused a decrease in conductivity and water uptake whereas oxidative stability was improved. For comparison, the proton conductivity of Nafion117 was measured with our test system and found as 133 mS cm^{-1}. For SPEEK70/Copolymer 1a–1b (95/5), SPEEK70/Copolymer 1a–1b (90/10) and SPEEK70/Copolymer 1a–1b (80/20) blend membranes conductivity values changed between 115.1 and 44.4 mS cm^{-1},
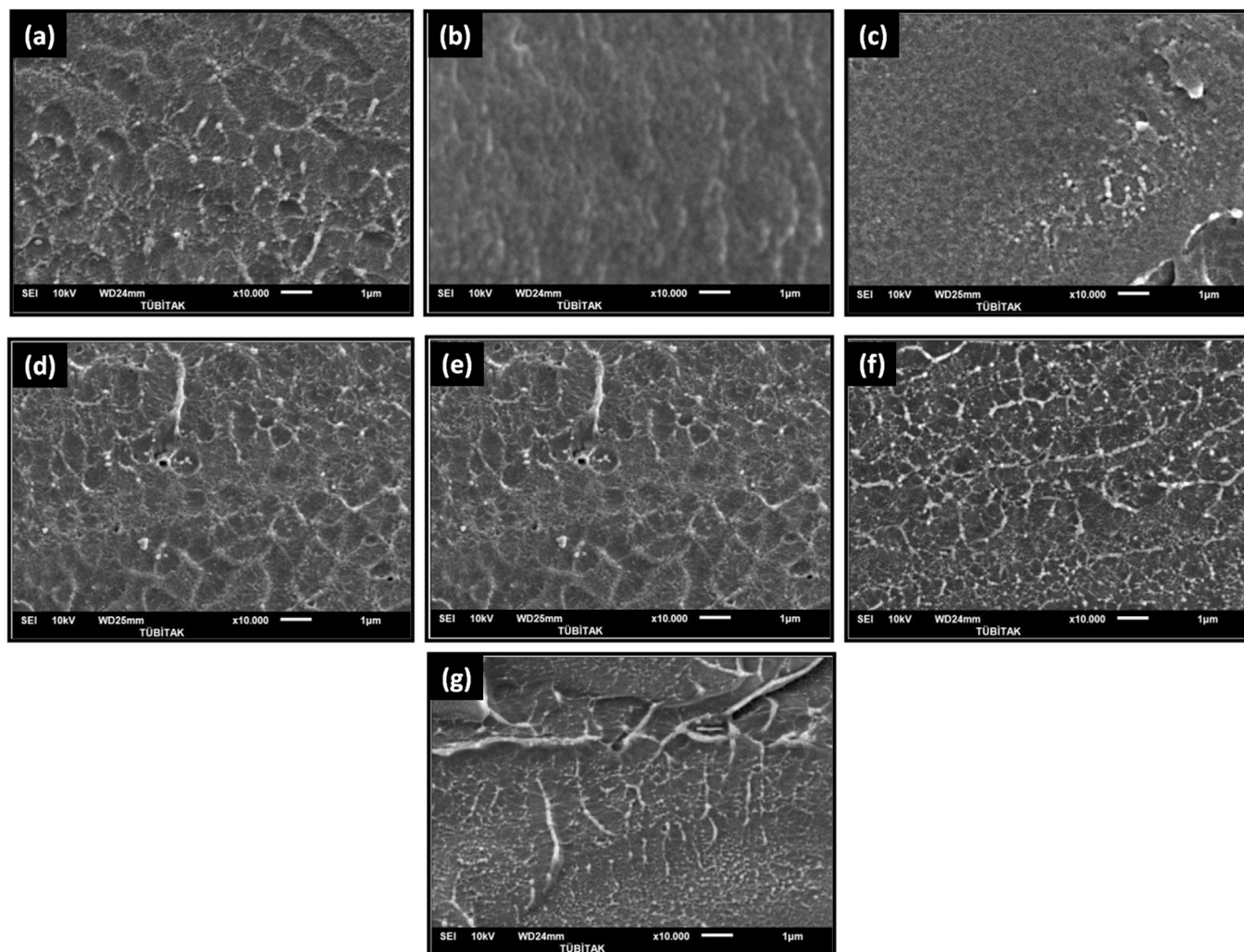
Fig. 7. SEM micrographs of the SPEEK70/Copolymers 1a and 1b blend membranes: (a) SPEEK70/Copolymer 1a: 95/5, (b) SPEEK70/Copolymer 1a: 90/10 (c) SPEEK70/Copolymer 1a: 80/20, (d) SPEEK70/Copolymer 1b: 95/5, (e) SPEEK70/Copolymer 1b: 90/10, (f) SPEEK70/Copolymer 1b: 80/20, (g) SPEEK70 (cross section).

94.6–36.9 mS cm^{-1} and 84.4–30.5 mS cm^{-1}, respectively. Proton conductivity decreased with the addition copolymer of 1a and 1b as expected due to decreased IEC and sulfonation degree by blending. Moreover, copolymer 1a containing blend membranes displayed higher proton conductivity than the copolymer 1b containing blend membranes. This might be because the former have higher IEC than the latter due to the molecular weight difference of related co-polymers. It is clear that, the proton conductivity of the sulfonated membranes was mainly influenced by IEC rather than the structure of copolymer. Moreover, it was supposed that, the copolymer 1a with Bis A structure favors better separation of the hydrophilic sulfonic acid groups from the hydrophobic main chain regions and thus improves the proton conductivity.

Additionally, the water uptake of SPEEK70 was measured as 28.8%. Generally, the water uptake of sulfonated polymers is strongly influenced by the degree of sulfonation or the ion exchange capacity of the polymer. For SPEEK70/Copolymer 1a–1b (95/5), (90/10) and (80/20) blend membranes, the water uptake values changed between 21.9 and 15.8%. The introduction of hydrophobic copolymer into the polymer backbone reduces the hydrophilicity of membrane due to the relatively low sulfonic acid group concentration in the blend. Moreover, CF$_3$ groups in copolymer 1b makes it more hydrophobic so the water uptakes for the copolymer 1b containing blends were the lowest ones. For example, while the SPEEK70/Copolymer 1a (80/20) blend membrane absorbed 19.1 wt.% of water at room temperature, the SPEEK70/Copolymer 1b (80/20) blend membrane shows a lower water uptake value of around 15.8 wt.%.

3.2.5. Oxidative stability

The oxidative stability to peroxide radical attack was evaluated by measuring the elapsed time just before the membrane breaks after its immersion in Fenton's reagent (3% H$_2$O$_2$ aqueous solution mixed with up to 4 ppm Fe^{2+}) at 68 °C [35] .The chemical stabilities of SPEEK70/Copolymer 1a and 1b blend membranes were improved with the addition of Copolymer 1a and 1b. SPEEK70/Copolymer 1a and SPEEK70/Copolymer 1b blend membranes were degraded completely in 6–6.5 h (Table 1) while the degradation time for SPEEK70 was measured only 2–2.5 h at the same conditions [21] .

However, it has been reported that fuel cell lifetime of poly-benzimidazoles (PBI) membranes was over 5000 h whereas average rupture time of these membranes determined by Fenton test was only 30 min [35–44]. Since Fenton test is an accelerated hydrolytic stability test, it exposes membrane to an unrealistic amount of radicals. Therefore a long-term durability test in fuel cell
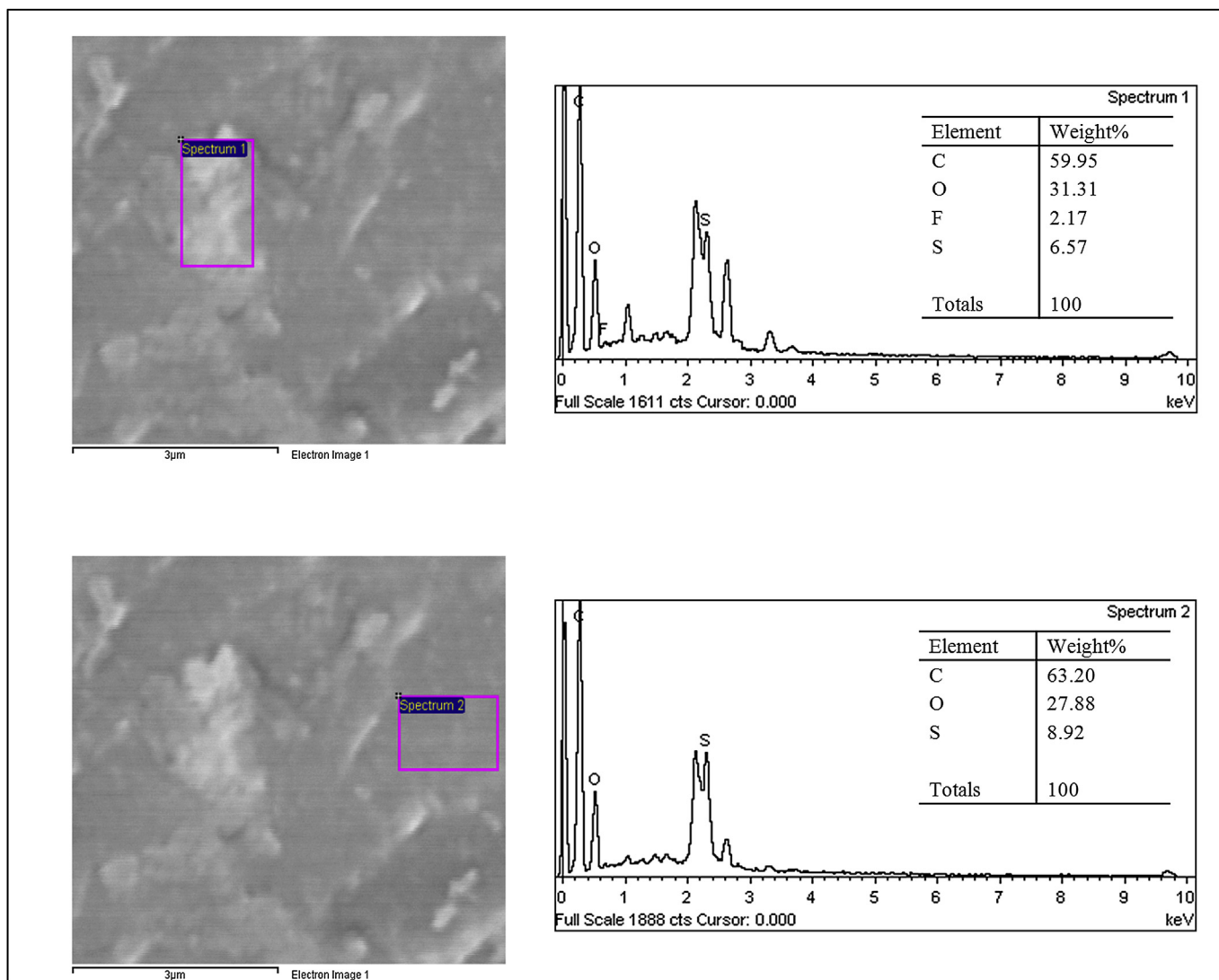
Fig. 8. EDS analysis results from SEM for SPEEK70/Copolymer 1a: 80/20 blend membrane.

must be also done substantially for determination of chemical stability of the membrane. Consequently, chemical stability of the SPEEK membranes with the addition of Copolymer 1a and 1b were improved when compared with values reported in the literature [38—47].

3.2.6. Gas permeability

The polymer electrolyte membrane requires gas sealing property which isolates fuels and oxidants respectively. Therefore low gas permeability is necessary. Fig. 13 shows gas permeability of the SPEEK70/Copolymer 1a (95/5) and SPEEK70/Copolymer 1b (95/5) blend membranes. SPEEK70/Copolymer 1a (95/5) (hydrogen permeability; 2.48×10^{-5} cm^3 s^{-1}, oxygen permeability; 1.57×10^{-5} cm^3 s^{-1}) and SPEEK70/Copolymer 1b (95/5) (hydrogen permeability; 2.23×10^{-5} cm^3 s^{-1}, oxygen permeability; 1.53×10^{-5} cm^3 s^{-1}) blend membranes showed lower hydrogen and oxygen permeability than that of Nafion® membrane (hydrogen permeability; 2.29×10^{-3} cm^3 s^{-1}, oxygen permeability; 6.64×10^{-4} cm^3 s^{-1}). These results prove that these membranes could be used for PEMFC and DMFC applications.

In literature mainly gas permeabilities measured at dried conditions and this article followed the same way. But in literature, it

was found also that "wet" or "dried gas permeability" values differ less than 10% as given in the PhD thesis of Minkmas Vatanatham Williams [49].

3.2.7. Mechanical properties of blend membranes

The mechanical properties of all the blends are shown in Table 2. With the increasing content of Copolymer 1a or 1b in SPEEK70, the tensile modulus of the membranes increased from 476.12—488.52 to 1051.71—1062.51 (1a), 1326.70—1338.9 (1b) MPa and the tensile strength increased from 9.21—19.01 to 13.09—15.69 (1a), 22.48—38.48 (1b) MPa. The more Copolymer 1a, 1b were added, the higher density and more compact membranes were obtained, which can be proved by SEM, the stronger functional materials were formed.

The elongation at break of SPEEK70 based blend membranes changed between 4 and 19 Mpa and Nafion (249 ± 0.5%) is much higher than that of blend membranes Addition of Florinated block copolymers to the SPEEK70 polymers caused decrease in elongation of the membranes and elongation of the Nafion is the highest (249%) of the membranes tested. Young modulus values of the blend membranes were also increased from 482 Mpa to 1332 Mpa depending on the ratio of the novel copolymer in the membrane
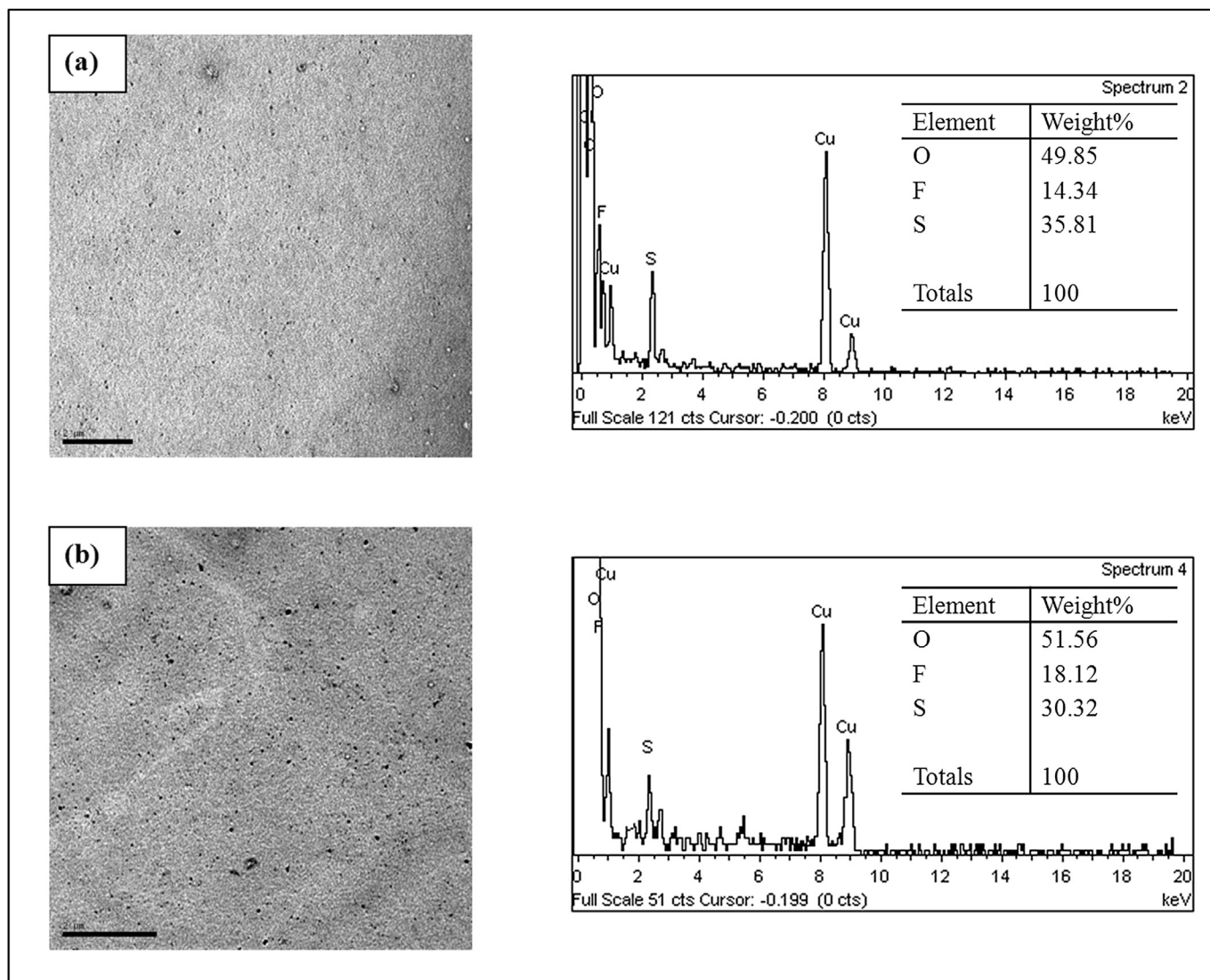
Fig. 9. EDS analysis result from TEM for SPEEK70/Copolymers 1a and 1b blend membranes: (a) SPEEK70/Copolymer 1a: 80/20, (b) SPEEK70/Copolymer 1b: 80/20.

and the structure of the polymer. The results obtained from Fenton test also supports the values obtained from mechanical testing. Because addition of novel polymers into the SPEEK70 based membranes definitely increased the decomposition values of the membranes from 2.5 h to 6–6.5 h. The membranes exhibited excellent mechanical properties, which indicated that the composite membranes are strong enough to be potential for usages in PEMFC.

3.2.8. Proton conductivity and methanol permeability

Fundamentally, membrane and fuel cell system design is an optimization effort driven by maximization of proton conductivity while minimizing methanol transport through the membrane. Increasing polymer ion exchange capacity (IEC), decreasing membrane thickness, changing fabrication or post-processing steps or controlling membrane hydration level can increase membrane conductivity, they also lead to increased methanol crossover [50].

Although methanol permeability of the pure SPEEK70 membrane (1.6×10^{-7} cm^2 s^{-1}) is considerably lower than that of the Nafion117 ($1,21 \times 10^{-6}$ cm^2 s^{-1}) membrane, further improvements made by blending with PVDF. For the blend membranes. In

literature, it was believed that the hydrophobic nature of PVDF restricts methanol solubility in the PVDF rich membranes [21,51].

The miscibility of polymer electrolyte blends also influences the transport properties. In Jeffrey V. et al's article, the phase behavior of PEI-SPEKK blends was strongly influenced by the sulfonation level of the SPEKK. At low IEC of SPEKK (0.8 meq g^{-1}), the blends were miscible, while at a slightly higher level (IEC 1.1 meq g^{-1}), they were only partially miscible and for IEC $\geq$ 1.4 meq g^{-1} they were effectively immiscible over the entire composition range. The PES-SPEKK blends were miscible over the entire range of SPEKK IEC (0.8–2.2 meq g^{-1}). At high IEC (2.2 meq g^{-1}) and at low mass fractions of SPEKK (<0.5), the miscible blends (PES-SPEKK) had higher proton conductivities and methanol permeabilities than the immiscible ones (PEI-SPEKK). The opposite relationship was observed for high mass fractions of SPEKK (>0.5) where both PEI-SPEKK and PES-SPEKK blend systems exhibited miscibility, the transport properties were not significantly different. This behavior was explained by the differences in morphology between these two blend systems [52].

For this case, SPEEK70/Novel polymer blends IEC's changed between 1.43 and 0.74 meq g^{-1} and the blend membranes were all miscible in all composition range. As sulfonated polymer of SPEEK
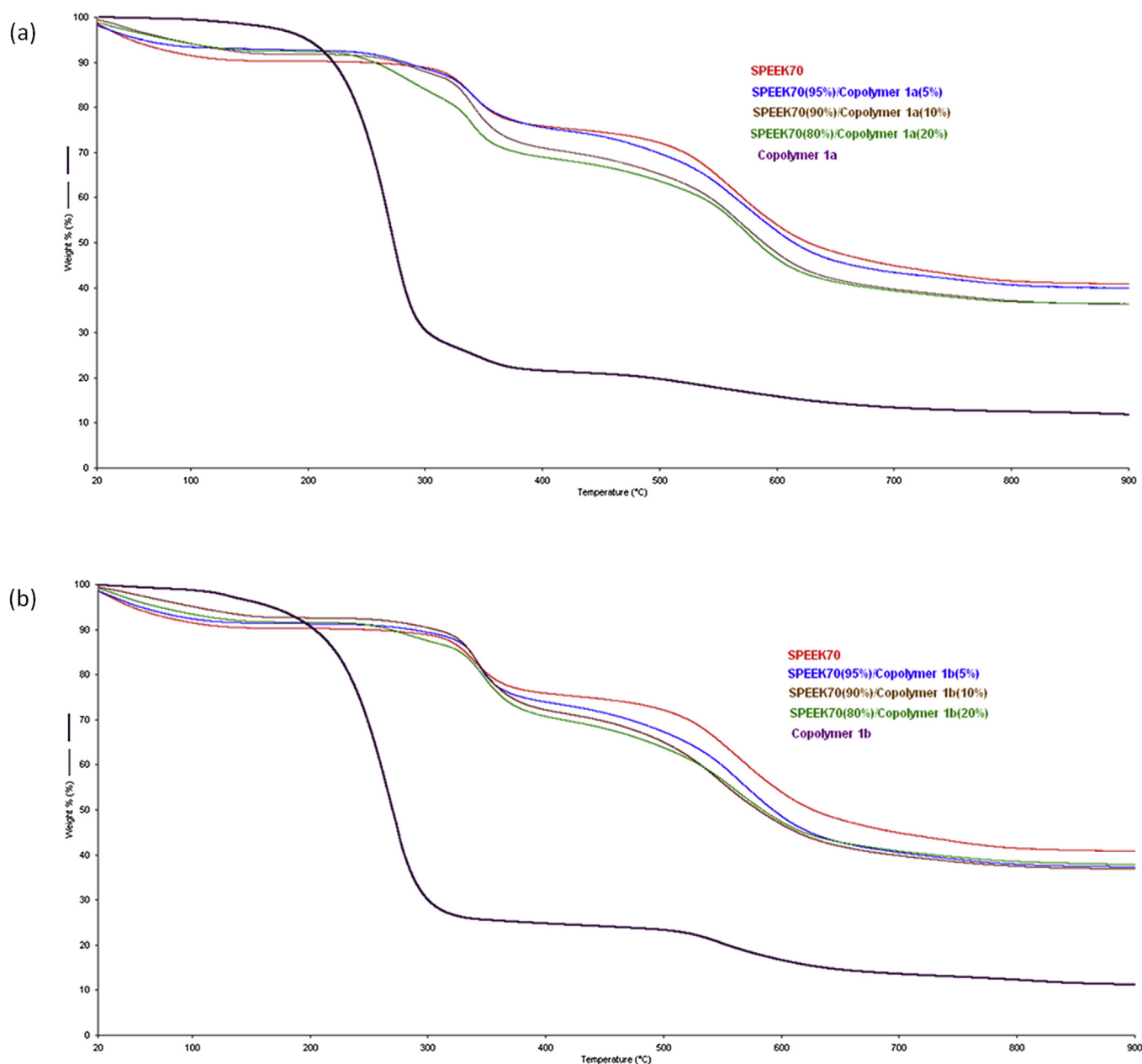
Fig. 10. TGA curves of (a) SPEEK70/Copolymer 1a and (b) SPEEK70/Copolymer 1b blend membranes.

composition increased, proton conductivity increased and addition of 20 wt.% of copolymer 1a and 1b into the system decreased methanol permeability values to 8.2×10^{-8} cm^2 s^{-1} and 1.3×10^{-9} cm^2 s^{-1} for copolymer 1a and copolymer 1b respectively and they were much lower than that of Nafion® 117 (1.21×10^{-6} (cm^2 s^{-1}) [48]. This behavior can be explained by the differences in morphology between these two blend systems. The blend with higher amount of flouride in its structure has lower methanol permeability and proton conductivity value. Fig. 14 shows proton conductivity and methanol permeability of the SPEEK70/Novel polymer blend membranes and increasing weight percentage of copolymer 1a and 1b in the blend membrane decreased the methanol permeability and also proton conductivity values. 10 wt.% addition of copolymers seemed to be critical for methanol permeability because below this ratio the methanol permeability is reliably high. The methanol permeability decreases with the

increasing of the copolymer content in the blend and reaches a plateau at about 10 wt.%. Therefore it can be concluded that for 10 and 20 wt.% of copolymer contents, a constancy in methanol permeability was obtained which was a necessity for the usability of this type of membranes as DMFC. On the other hand, methanol-water solubility findings as given in 3.2.9 showed that blend systems have less weight loses than Nafion117 and all these results support that these membranes are resistant to methanol permeability and suitable for DMFC applications.

3.2.9. Methanol—water solubility test

To perform methanol—water solubility test 50/50 wt.% methanol—water solution was prepared. Nafion117, well known membrane, is taken as a standard material in our study. Fig. 15 shows the solubility of the blend membranes at 80 °C for 24 h. With increasing copolymer content in polymer blends, the weight loss values
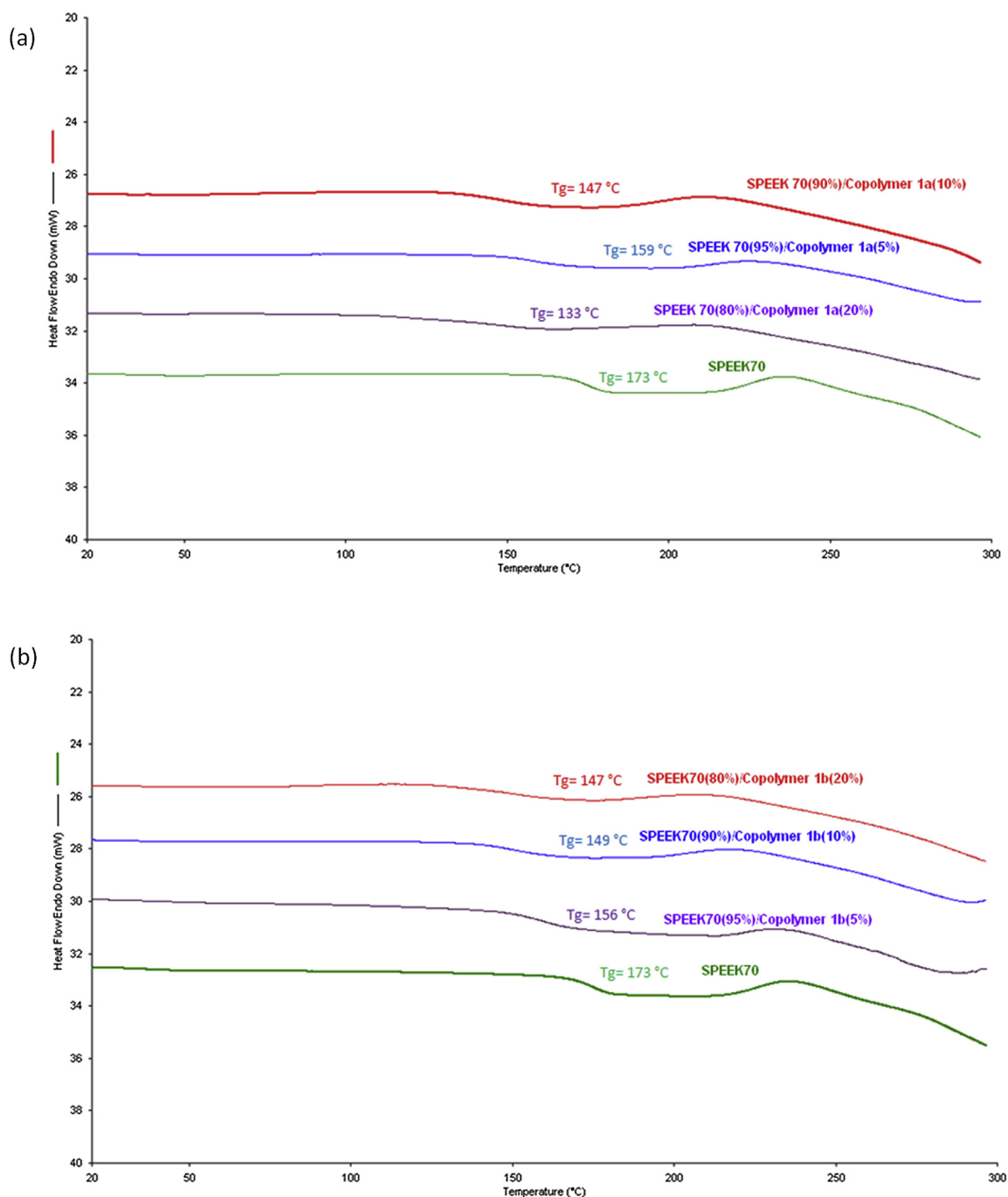
Fig. 11. DSC curves of (a) SPEEK70/Copolymer 1a and (b) SPEEK70/Copolymer 1b blend membranes.

increases from 28.7 to 39.5 wt.% for Copolymer 1a and from 35.1 to 37 for Copolymer 1b, respectively. For Nafion117, weight loss was greater than 60% at the same conditions.

3.2.10. Water vapor permeability

Water vapor transmission through proton exchange membranes is important for fuel cell operation and the water vapor permeance shows water transportation degree through the membrane. A high water vapor permeance means higher diffusion of the water through the membrane during fuel cell operation, which could lead to a more uniform distribution of water during fuel cell operation [53].

Water vapor transmission and permeability values of SPEEK70, Nafion and SPEEK70/Copolymer 1a, 1b blend membranes were presented in Table 3. Nafion has the highest value of water vapor transmission. SPEEK70/Copolymer 1a (90/10) and (80/20) blend membranes were exhibited lower vapor permeability than pristine SPEEK70. However, addition of hydrophobic polymer of copolymer 1b to the SPEEK70 polymer matrix in 10−20 wt.% caused increase in water vapor transmission.

Table 1
Properties of SPEEK70/Copolymer 1a, 1b based membranes.

Membrane	$IEC_m{}^a$ (meq g^{-1})	WU^b (wt.%)	Fenton test $t_{decomp}{}^c$ (h)	σ^d (mS cm^{-1})
SPEEK70	1.43	28.8	2.5	156.1
SPEEK70/Copolymer 1a (95/5)	1.24	21.6	6.5	115.1
SPEEK70/Copolymer 1a (90/10)	0.93	20.0	6.5	94.6
SPEEK70/Copolymer 1a (80/20)	0.85	19.1	6.5	84.4
SPEEK70/Copolymer 1b (95/5)	1.02	21.9	6.0	44.4
SPEEK70/Copolymer 1b (90/10)	0.89	17.4	6.0	36.9
SPEEK70/Copolymer 1b (80/20)	0.74	15.8	6.0	30.5

[a] IEC_m: Membranes ion exchange capacity, meq g^{-1}.
[b] WU: Water uptake of membranes, wt.%.
[c] WL: Decomposition time from Fenton test, h.
[d] σ: Proton conductivity at 80 °C, %100 RH, mS cm^{-1}.

Fig. 13. Hydrogen and oxygen permeability of the membranes.

Table 2
The mechanical properties of the composite membranes.

Composite membranes	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
SPEEK70	482.32 ± 6.2	14.11 ± 4.9	19.33 ± 4.3
SPEEK70(95%)/Copolymer 1a(5%)	560.87 ± 5.1	11.67 ± 2.2	7.33 ± 1.9
SPEEK70(90%)/Copolymer 1a(10%)	732.13 ± 6.8	14.06 ± 2.1	6.02 ± 0.8
SPEEK70(80%)/Copolymer 1a(20%)	1057.11 ± 5.4	14.39 ± 1.3	5.65 ± 2.2
SPEEK70(95%)/Copolymer 1b(5%)	707.53 ± 4.7	7.09 ± 4.4	7.98 ± 0.6
SPEEK70(90%)/Copolymer 1b(10%)	739.34 ± 5.2	7.51 ± 2.6	4.75 ± 1.2
SPEEK70(80%)/Copolymer 1b(20%)	1332.80 ± 6.1	30.48 ± 8.0	3.74 ± 2.1

4. Conclusions

Phosphine oxide containing flourinated monomer was synthesized and it was used to synthesize two new poly(arylene ether) copolymers (1a-1b). Homogeneous blend membranes of sulfonated poly(etherether ketone) (SPEEK) with sulfonation degree of 70 and copolymers 1a and 1b with the ratios of 5—20 wt.% were prepared using solvent casting method. The obtained blend membranes due to their flourinated structure with higher bond strength of the C—F bond showed high chemical, mechanical, and hydrolytic stability. Chemical stabilities of the blend membranes improved from 2.5 h to 6.6 h by the addition of fluorinated polymer which is the highest value for SPEEK/flourinated polymer blends in the literature. In
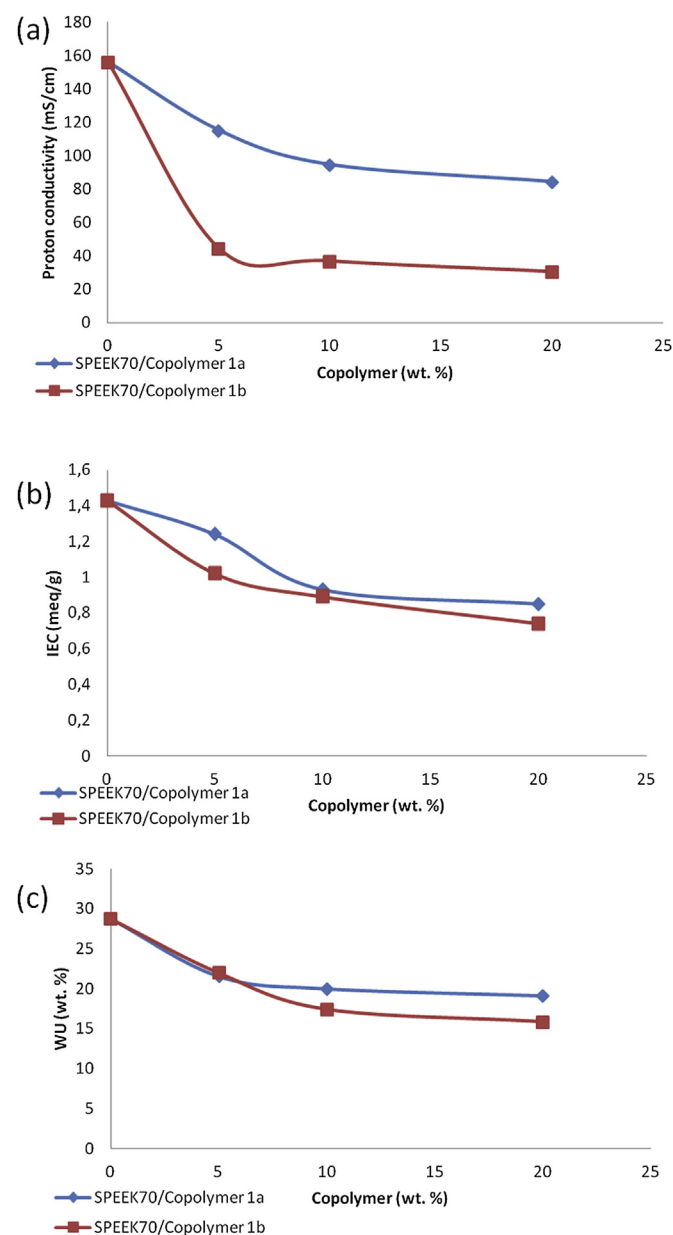

Fig. 12. Proton conductivity ($T = 80$ °C, RH = 100%), IEC and water uptakes of SPEEK70/ Copolymer 1a, 1b blend membranes with different concentrations.
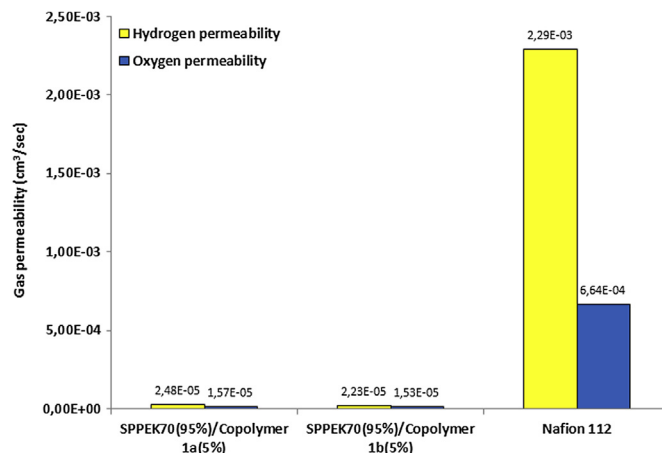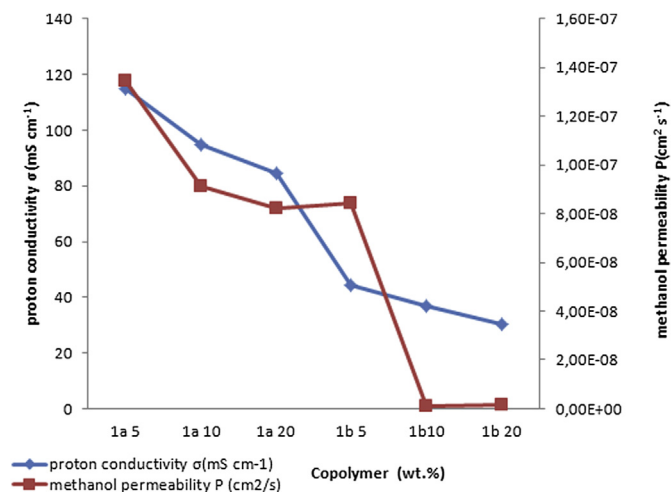

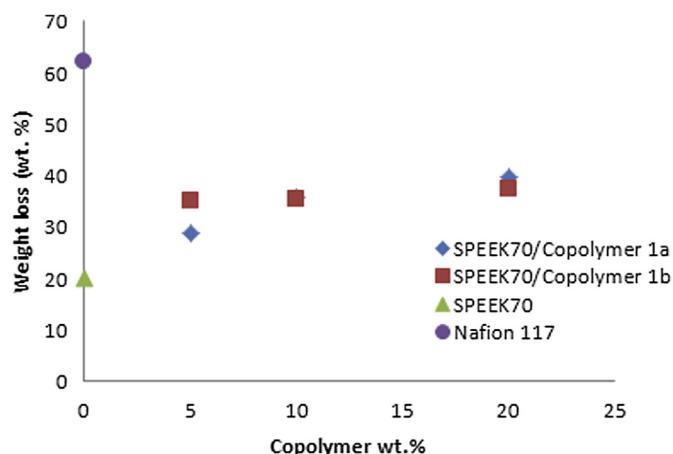**Fig. 14.** Proton conductivity and methanol permeability of the membranes.

Fig. 15. Methanol–water solubility test of membranes.

Table 3
Water vapor transmission and permeability of blend membranes.

	WVTR (g m^{-2} h^{-1})	WVP (g m^{-1} s^{-1} Pa^{-1})
SPEEK70	12.1	1.6×10^{-10}
SPEEK70/Copolymer 1a (90/10)	10.4	8.3×10^{-11}
SPEEK70/Copolymer 1a (80/20)	11.0	1.2×10^{-10}
SPEEK70/Copolymer 1b (90/10)	12.7	2.5×10^{-10}
SPEEK70/Copolymer 1b (80/20)	13.3	2.2×10^{-10}
Nafion® 117	17.9	5.6×10^{-10}

addition phenyl phosphine oxide moiety in the structure increased the thermal stability. Their hydrogen and oxygen permeability values determined as one-hundredth of the Nafion® much lower than that of Nafion® 112. They also showed lower water vapor permeability than that of Nafion® membrane. Methanol permeability values of blend membranes were much lower than Nafion® 117 membrane (Nafion® 117: 1.21×10^{-6} cm^2 s^{-1}; copolymer 1a: 8.2×10^{-8} cm^2 s^{-1} and copolymer 1b: 1.3×10^{-9} cm^2 s^{-1}) and methanol-water solubility findings also showed that blend systems have less weight loses than Nafion® 117. Their water uptake and proton conductivity values decreased with the addition of fluorinated polymers as expected, but the values were still close to the Nafion® membrane. Low and stable methanol permeability was obtained for 10 and 20 wt.% of copolymer containing blends, which was a necessity for the usability of this type of membranes as proton exchange membranes. In terms of water uptake and proton conductivity, although the blend membranes in the present study were close to those of the Nafion® membrane, the methanol permeability is effectively lower than that of Nafion®. Considering all the performance results of the blend membranes with two novel flourinated polymers, we could conclude that the SPEEK70/Copolymer 1a, 1b blend membranes are promising either for different type of fuel cell applications (DMFC, PEMFC).

Acknowledgment

References

[1] D.W. Seo, Y.D. Lim, S.H. Lee, Md. M. Islam, H.M. Jin, K.H. Lee, H.H. Jang, W.G. Kim, Mater. Sci. Forum 658 (2010) 392–395.
[2] Y. Shao, G. Yin, Z. Wang, Y. Gao, J. Power Sources 167 (2007) 235–242.
[3] V. Mehta, J.S. Cooper, J. Power Sources 114 (2003) 32–53.
[4] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Chem. Mater. 15 (2003) 4896–4915.
[5] A.L. Rusanov, D. Likhatchev, P.V. Kostoglodov, K. Müllen, M. Klapper, Adv. Polym. Sci. 179 (2005) 83–134.
[6] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587–4612.
[7] N. Miyake, J.S. Wainright, R.F. Savinell, J. Electrochem. Soc. 148 (2001) A905–A909.
[8] J.Y. Park, T.H. Kim, H.J. Kim, J.H. Choi, Y.T. Hong, Int. J. Hydrogen Energy 37 (2012) 2603–2613.
[9] J.A. Kerres, D. Xing, F. Schonberger, J. Polym. Sci. Part B Polym. Phys. 44 (2006) 2311–2326.
[10] Y. Chen, R. Guo, C. Hyun Lee, M. Lee, J.E. McGrath, Int. J. Hydrogen Energy 37 (2012) 6132–6139.
[11] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.
[12] Y.S. Kim, M.J. Sumner, W.L. Harrison, J.S. Riffle, J.E. McGrath, B.S. Pivovar, J. Electrochem. Soc. 151 (2004) A2150–A2156.
[13] J. Kerres, W. Zhang, L. Jörissen, V. Gogel, J. New Mater. Electrochem. Syst. 5 (2002) 97–107.
[14] F. Schönberger, M. Hein, J. Kerres, Solid State Ionics 178 (2007) 547–554.
[15] F.G. Wilhelm, I.G.M. Punt, N.F.A. van der Vegt, H. Strathmann, M. Wessling, J. Membr. Sci. 199 (2002) 167–176.
[16] J. Kerres, J. Membr. Sci. 185 (2001) 3–27.
[17] Polymer Material for Electrolytic Membranes in Fuel Cells, 1998, US 5 795 496.
[18] S.D. Mikhailenko, S.M.J. Zaidi, S. Kaliaguine, J. Polym. Sci. Part B Polym. Phys. 38 (2000) 1386–1395.
[19] C. Manea, M. Mulder, J. Membr. Sci. 206 (2002) 443–453.
[20] D. Daoust, J. Devaux, P. Godard, A. Jonas, R. Legras, in: H. Kausch (Ed.), Advanced Thermoplastic Composites—Characterization and Processing, Carl Hanser, Munich, 1992 (Chapter 1).
[21] T.Y. İnan, H. Doğan, E.E. Ünveren, E. Ersoy, Int. J. Hydrogen Energy 35 (2010) 12038–12053.
[22] H.L. Wu, C.C.M. Ma, H.C. Kuan, C.H. Wang, C.Y. Chen, C.L. Chiang, J. Polym. Sci. Part B Polym. Phys. 44 (2006) 565–572.
[23] S. Hirose, K. Nakamura, T. Hatakeyama, H. Hatakeyama, Sen-i Gakkaishi 43 (1987) 595–600.
[24] X. Ma, C. Zhang, G. Xiao, D. Yan, G. Sun, J. Polym. Sci. Part A Polym. Chem. 46 (2008) 1758–1769.
[25] J.A. Kerres, D. Xing, F. Schönberger, J. Membr. Sci. 33 (2006) 280–501.
[26] R.A. Weiss, A. Sen, C.L. Willis, L.A. Pottick, Polymer 32 (1991) 1867–1874.
[27] L. Zhang, S. Mukerjee, J. Electrochem. Soc. 153A (2006) 1062–1072.
[28] X. Zhang, PhD Thesis, Spain: Department of Chemical Engineering, Universitat Rovira i Virgili (URV), October 2005.
[29] J.-S. Park, P. Krishnan, S.-H. Park, G.-G. Park, T.-H. Yang, W.-Y. Lee, J. Power Sources 178 (2008) 642–650.
[30] H.D. Moore, T. Saitoab, M.A. Hickner, J. Mater. Chem. 20 (2010) 6316–6321.
[31] Y. Zhao, J. Yin, J. Membr. Sci. 351 (2010) 28–35.
[32] Z. Liyuan, Z. Gang, Z. Chengji, L. Zhongguo, J. Hao, X. Shuai, L. Mingyu, X. Dan, N. Hui, Int. J. Hydrogen Energy 38 (2013) 12363–12373.
[33] X.H. Ye, H. Bai, W.S.W. Ho, J. Membr. Sci. 279 (2006) 570–577.
[34] Z. Wang, X.F. Li, C.J. Zhao, H.Z. Ni, H. Na, J. Power Sources 160 (2006) 969–976.
[35] S. Zhong, X. Cui, H. Cai, T. Fu, K. Shao, H. Na, J. Power Sources 168 (2007) 154–161.
[36] A.B. LaConti, M. Hamdan, R.C. McDonald, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), Handbook of Fuel Cells: Fundamentals, Technology, John Wiley & Sons, Ltd., New York, 2003, pp. 647–662.
[37] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Fuel Cells 4 (2004) 147–159.
[38] C. Bailly, D.J. Williams, F.E. Karasız, W.J. MacKnight, Polymer 26 (1987) 1009–1016.
[39] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, J. Membr. Sci. 229 (2004) 95–106.
[40] J.A. Dias, E. Caliman, S.C.L. Sias, Microporous Meseoporous Mater. 76 (2004) 221–232.
[41] S. Choi, Y. Wang, Z. Nie, J. Liu, C.H.F. Peden, Catal. Today 55 (2000) 117–124.
[42] N. Essayem, A. Holmqvist, P.Y. Gayraud, J.C. Vedrine, Y. Ben Taarit, J. Catal. 197 (2001) 273–280.
[43] D. Zhaoa, B.L. Yia, H.M. Zhang, H.M. Yuc, L. Wang, Y.W. Ma, J. Power Sources 190 (2008) 301–306.
[44] A. Ghanbari-Siahkali, A. Philippou, J. Dwyer, M.W. Anderson, Appl. Catal. A 192 (2000) 57–69.
[45] L. Li, L. Xu, Y. Wang, Mater. Lett. 57 (2003) 1406–1410.
[46] B. Smitha, S. Sridhar, A.A. Khan, J. Membr. Sci. 225 (2003) 63–76.
[47] L. Zhang, S. Mukerjee, J. Electrochem. Soc. 153 (2006) A1062–1072.
[48] S.-W. Chuang, S.L.-C. HSu, J. Polym. Sci. Part A Polym. Chem. 44 (2006) 4508–4513.
[49] M.V. Williams, Chemical Engineering (PhD Thesis), University of Connecticut, 2004.
[50] L. Beer, D.L. Olmeijer, M.C. Lefebvre, in: , 216th ECS Meeting, Abstract − 1093, The Electrochem. Soc., 2009.
[51] J. Wootthikanokkhan, N. Seeponkai, J. Appl. Polym. Sci. 102 (2006) 5941–5947.
[52] J.V. Gasa, R.A. Weıss, M.T. Shaw, J. Polym. Sci. Part B Polym. Phys. 44 (2006) 2253–2266.
[53] H. Doğan, T.Y. Inan, E. Unveren, M. Kaya, Int. J. Hydrogen Energy 35 (2010) 7784–7795.